ANTI-MICROBIAL FIBER AND FIBROUS PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a divisional application of Serial No. 09/565,138 filed May 5, 2000 which claims the priority of the following provisional applications: Serial No. 60/136,261, filed May 27, 1999; Serial No. 60/173,207, filed December 27, 1999; Serial No. 60/172,285, filed December 17, 1999; Serial No. 60/172,533, filed December 17, 1999; Serial No. 60/180,536, filed February 7, 2000; Serial No. 60/181,251, filed February 9, 2000; and Serial No. 60/180,240, filed February 4, 2000.

FIELD OF THE INVENTION

[0010] The present invention relates generally to products having anti-microbial (and/or anti-fungal) properties which remain with the product after repeated launderings/uses. More specifically it provides laminate materials that are made of a wholly thermoplastic stiff reinforcing multiple laminate moldable into compound shapes and bondable via a thermoplastic hot melt adhesive to a carrier surface to be reinforced and suitable for footwear.

BACKGROUND OF THE INVENTION

[0011] There is a growing interest today in products which have anti-microbial and anti-fungal properties. There are a number of additives, fibers and products on the market which claim to have these properties. However, many do not have such properties, or the properties do not remain for the life of the product, or they have adverse environmental consequences.

[0012] Various materials have been used in the past to provide anti-microbial and anti-fungal properties to fibers and fabrics.

[0013] Examples of some organic types of anti-microbial agents, are U.S. Patents Nos.: 5,408,022 and 5,494,987 (an anti-microbial polymerizable composition containing an ethylenically unsaturated monomer, a specific one-, di- or tri-functional anti-microbial monomer and a polymerization initiator which can yield an unreleasable anti-microbial polymer from which the anti-microbial component is not released), 5,709,870 (a silver containing anti-microbial agent

which comprises carboxymethylcellulose, a crosslinked compound, containing silver in the amount of .01 to 1% by weight and having a degree of substitution of carboxymethyl group of not less than .4 and the anti-microbial agent being a silver salt of carboxymethylcellulose, which is insoluble to water), 5,783,570 (an organic solvent-soluble mucopolysaccharide consisting of an ionic complex of at least one mucopolysaccharide and a quaternary phosphonium, an antibacterial antithrombogenic composition comprising organic solvent-soluble mucopolysaccharide and an organic polymer material, an antibacterial antithrombogenic composition comprising organic solvent-soluble mucopolysaccharide and an inorganic antibacterial agent, and to a medical material comprising organic solvent-soluble mucopolysaccharide).

[0014] Examples of some inorganic types of anti-microbial agents are:

[0015] Japanese Patent No. 1246204 (1988) which discloses an anti-microbial thermoplastic article with copper a compound added to the melted polymer just before extruding, in which the anti-microbial material is said to be resistant to washing.

[0016] U.S. Patent No. 5,180,585 which discloses an antimicrobial with a first coating providing the antimicrobial properties and a second coating as a protective layer. A metal having antimicrobial properties is used including silver which is coated with a secondary protective layer.

[0017] Japanese Patent No. 2099606 (1990) which discloses a fiber with anti-microbial properties made of a liquid polyester and inorganic micro particles of zinc silicate, both being added to the melted polymer after polymerization and just before extrusion.

[0018] The use of anti-microbial agents in connection with thermoplastic material is known from U.S. Patent No. 4,624,679 (1986). This patent is concerned with the degradation of anti-microbial agents during processing. This patent states that thermoplastic compounds which are candidates for treatment with anti-microbial agents include material such as polyamides (nylon 6 or 6,6), polyvinyl, polyolefins, polyurethanes, polyethylene terephthalate, styrene-butadiene rubbers.

[0019] Japanese Patent No. 2091009 (1990) and U.S. Pat No 5,047,448 disclose an anti-microbial thermoplastic polymer with copper or zinc compounds and fine particles of Al, Ag, Fe

and Zn compounds and a liquid polyester, in which the anti-microbial material is said to be resistant to washing.

[0020] Japanese Patent No. 2169740 (1990) discloses a thermoplastic fiber such as PET which uses silver, copper or zinc as an anti-microbial agent. There is a cellulose component which reduces the amount of thermoplastic with anti-microbial agent and reduces the cost.

[0021] Examples of inorganic types of anti-microbial agent which have zeolite with silver is disclosed in U.S. Patents Nos. 4,911,898 , 5,094,847, 4,938,958 (use of zeolite with exchangeable ions such as silver and others), 5,244,667 (an anti-microbial composition which involves use of partial or complete substitution of ion-exchangeable metal ion such a silver, copper, zinc and others), 5,405,644 (an anti-microbial fiber having a silver containing inorganic microbiocide and the silver ion is stated to have been supported by zeolite, among other materials, the purpose being to prevent discoloration).

[0022] Japanese Patent No. 6116872 (1994) discloses a suede-like synthetic leather with an anti-microbial agent. It discloses the use of anti-microbial zeolite having an anti-microbial metal ion. It uses two fiber types and includes PET.

[0023] U.S. Patent No. 5,733,949 discloses an anti-microbial adhesive composition for dental use. The composition was made by blending of a polymerizable monomer having alcoholic hydroxy group and water to a dental composition containing an anti-microbial polymerizable monomer and a polymerizable monomer having acidic group, and with a polymerization catalyst. Such composition has capability to improve adhesive strength between the tooth and the restorative material to prevent microbial invasion at the interface and kill microorganisms remaining in the microstructure.

[0024] U.S. Patent No. 5,876,489 discloses a germ-removing filter with a filter substrate and an anti-microbial material dispersedly mixed into the filter substrate. The anti-microbial material is an ion exchange fiber bonded with silver ion. In the ion exchange fiber, silver ions capable of killing living germs through an ion exchange reaction.

[0025] U.S. Patent No. 5,900,258 discloses a method for preventing a microorganism from growing and the breakdown of urea to ammonia on the surface of skin, wall, floor, countertop or

wall covering, or in absorbent materials by incorporating an effective amount of naturally-occurring and/or synthetic zeolites. The absorbent materials are diapers, clothing, bedsheets, bedpads, surgical apparel, blankets, filters, filtering aids, wall coverings, countertops, and cutting boards, etc. Use of zeolite preventing bacterial infections and rashes in mammals may compromise cell wall processes including basic transport processes. Zeolites may capture or neutralize electrons and inhibit electron transport through key enzymes of the electron transport chain such as cytochrome oxidase.

[0026] PETG as used herein means an amorphous polyester of terephthalic acid and a mixture of predominately ethylene glycol and a lesser amount of 1,4-cyclohexanedimethanol. It is known that PETG can be used in polycarbonate blends to improve impact strength, transparency, processability, solvent resistance and environmental stress cracking resistance.

[0027] Udipi discloses in U.S. Patents Nos. 5,104,934 and 5,187,228 that polymer blends consisting essentially of PC, PETG and a graft rubber composition, can be useful as thermoplastic injection molding resins.

[0028] Chen et al. in U.S. Patent No. 5,106,897 discloses a method for improving the low temperature impact strength of a thermoplastic polyblend of PETG and SAN with no adverse effect on the polyblends clarity. The polyblends are useful in a wide variety of applications including low temperature applications.

[0029] Billovits et al. in U.S. Patent No. 5,134,201 discloses that miscible blends of a thermoplastic methylol polyester and a linear, saturated polyester or co-polyester of aromatic dicarboxylic acid, such as PETG and PET, have improved clarity and exhibit an enhanced barrier to oxygen relative to PET and PETG.

[0030] Batdorf in U.S. Patent No. 5,268,203 discloses a method of thermoforming thermoplastic substrates wherein an integral coating is formed on the thermoplastic substrate that is resistant to removal of the coating. The coating composition employs, in a solvent base, a pigment and a thermoplastic material compatible with the to-be-coated thermoplastic substrate. The thermoplastic material, in cooperation with the pigment, solvent and other components of the coating composition, are, after coating on the thermoplastic substrate, heated to a thermoforming

temperature and the thermoplastic material is intimately fused to the thermoplastic substrate surface.

[0031] Ogoe et al. in U.S. Patent No. 5,525,651 disclose that a blend of polycarbonate and chlorinated polyethylene has a desirable balance of impact and ignition resistance properties, and useful in the production of films, fibers, extruded sheets, multi-layer laminates, and the like.

[0032] Hanes in U.S. Patent No. 5,756,578 discloses that a polymer blend comprising a monovinylarene/conjugated diene black copolymer, an amorphous poly(ethylene terephthalate), e.g. PETG, and a crystalline poly(ethylene terephthalate), e.g. PET, has a combination of good clarity, stiffness and toughness.

[0033] Eckart et al. in U.S. Patent No. 5,958,539 disclose a novel thermoplastic article, typically in the form of sheet material, having a fabric comprising textile fibers embedded therein. The thermoplastic article is obtained by applying heat and pressure to a laminate comprising an upper sheet material, a fabric comprised of textile fibers and a lower sheet material. The upper and lower sheet materials are formed from a co-polyester, e.g. PETG. This thermoplastic article may be used in the construction industry as glazing for windows. One or both surface of the article may be textured during the formation of the articles.

[0034] Ellison in U.S. Patent No. 5,985,079 discloses a flexible composite surfacing film for providing a substrate with desired surface characteristics and a method for producing this film. The film comprises a flexible temporary carrier film and a flexible transparent outer polymer clear coat layer releasably bonded to the temporary carrier film. A pigment base coat layer is adhered to the outer clear coat layer and is visible there through, and a thermo-formable backing layer is adhered to the pigmented base coat layer. The film is produced by extruding a molten transparent thermoplastic polymer and applying the polymer to a flexible temporary carrier thereby forming a continuous thin transparent film. The formed composite may be heated while the transparent thermoplastic polymer film is bonded to the flexible temporary carrier to evaporate the volatile liquid vehicle and form a pigment polymer layer. The heating step also molecularly relaxes the underlying film of transparent thermoplastic polymer to relieve any molecular orientation caused by the extrusion. Ellison also mentions that it is desirable to form the flexible temporary carrier

from a material that can withstand the molten temperature of the transparent thermoplastic polymer. The preferred flexible temporary carriers used in his invention are PET and PETG.

[0035] Currently, many tee shirts, such as the grey athletic shirts, are made by blending in up to 10% of either solution dyed black polyester or stock dyed cotton. The solution dyed polyester has a disadvantage in that the product can no longer be labeled 100% cotton. The stock dyed cotton has the disadvantage in that it is not color fast, especially to bleach, and that it needs to be passed through a dye bath.

[0036] While anti-microbial agents are known in the footwear art, the agents used in these applications are generally organic substances. The disadvantage of these organic agents when used as anti-microbial agents is that bacteria can develop a resistance to their action. Thus, one is faced with the emergence of bacterial strains that are no longer affected by these anti-microbial agents which negates the function of these materials, and is harmful to humans since they are resistant to antibiotics.

[0037] One type of known shoe component is an insole disclosed in U.S. Patent No. 4,864,740 for Disposable Insoles, which includes three layers in which the anti-microbial agent is placed into the middle layer. As an alternative, the anti-microbial can be placed into the other layers, disclosing that the particular layer into which the anti-microbial agent is used is not important.

[0038] U.S. Patent No. 4,401,770 for Shoe Insole Having Anti-bacterial and Anti-fungal Properties is a flexible polyurethane foam prepared from a reaction mixture incorporating an anti-bacterial and anti-fungal agent which is a pyridinethione compound. The agent is introduced into the product and is the same concentration throughout the product.

[0039] Thus, there still exists a need to develop anti-microbial footwear components that do not cause the development of resistant bacterial strains. There also still exists a need for these components to have anti-microbial agent systems that are resistant to being worn away by abrasion, thus maintaining their potency as an integral part of the footwear components into which they are incorporated.

[0040] Sheet materials for various uses are vulnerable to the seeding of bacteria and fungi from various sources, thus providing hospitable sites for their uninhibited growth. The latter is especially true since, depending upon the end use, they often are used in environments where there is great exposure to microbes and fungi. One example is cafeteria trays. Thus, these materials would benefit from having antibacterial and anti-fungal agents incorporated onto them and/or into them. However, most prior art approaches of providing sheet materials with anti-microbial or anti-fungal agents have limited effect.

[0041] A variety of patents relate to anti-microbial materials being added to materials. For example, U.S. Patent No. 3,959,556 (1976) relates to synthetic fibers that incorporate an anti-microbial agent. U.S. Patent No. 4,624,679 (1986) , mentioned above, uses anti-microbial agents in connection with thermoplastic materials. These materials are formed by mixing polyamide resins, anti-microbial agents, and an antioxidant for reducing the degradation of the anti-microbial agent at the high temperatures necessary for processing.

[0042] Several other patents describe anti-microbial materials in which the anti-microbial agent is resistant to being washed away. U.S. Patent No. 4,919,998 (1990) discloses an anti-microbial material that retains its desirable properties after repeated washings.

[0043] However, these materials have two inherent commercial disadvantages. First, while the anti-microbial agents incorporated into them do show some resistance to repeated washings, these agents do leach out of the materials, primarily because they are not physically incorporated into them. In fact, in many cases, the anti-microbial agents are only loosely bound into the material and are relatively easily washed away or naturally abraded away over time.

[0044] On the other hand if the agents are buried too deeply in the material or homogeneously distributed they will not contact microbes at all and the economics of usage will be adversely affected.

[0045] Second, the anti-microbial agents used in these applications are generally organic substances. The disadvantage of these agents when used as anti-microbial agents is that bacteria can develop a resistance to their action. Thus, one is faced with the emergence of bacterial strains

that are no longer affected by these anti-microbial agents which negates the function of these materials.

[0046] U.S. Patent No. 4,923,914 for a Surface-Segregatable, Melt-Extrudable Thermoplastic Composition discloses forming a fiber or film of polymer and an additive in which the additive concentration is greater at the surface. for example when surfactants are added to polymers to impart a special property thereto such as a hydrophilic character to the surface, if the additive is compatible with the polymer there is a uniform concentration of the additive throughout the polymer. In the past such webs have been bloomed to bring the surfactant to the surface. But the surfactant is incompatible at melt-extrusion temperatures. The patentee describes a process for overcoming this problem.

[0047] However, the process described has not been very usable with anti-microbial agents. For example, see U. S. Patent No. 5,280,167 which describes the '914 patent discussed above and states that previous attempts to apply the teachings thereof to the preparation of non-woven webs having anti-microbial activity were not successful. This '167 patent provides for delayed anti-microbial activity in order to delay the segregation characteristic of the '914 patent from occurring. The additive which is used is a siloxane quaternary ammonium salt, an organic material.

[0048] While these anti-microbial agents are designed to prevent the development of resistant bacterial strains, the use of metal-containing materials presents the added difficulty of being able to successfully disperse the anti-microbial agents throughout the material. Since these metal-containing compounds exists as fairly large size particles (10 microns and greater), the ability to evenly mix or distribute them is limited. In addition, because of this size problem, these substances must necessarily be applied to the surfaces of materials instead of being incorporated into them. The latter causes the additional disadvantage of making the applied anti-microbial agents relatively labile to washings or abrasion.

[0049] U.S. Patent No. 4,350,732 for reinforcing laminate which issued September 21, 1982 discusses a moldable laminate which could be molded into curved shapes and which is bondable

to a carrier surface and which is useful in the making of military boots and the like. The present invention is an improvement.

[0050] Institutional furnishings are subject to excessive wear and tear. These furnishings must withstand the constant onslaught of dirt and spills of a variety of substances. They must also stand up to frequent cleanings with industrial strength cleansers. As a result, these furnishings could be made stronger and more resistant by using anti-microbial and anti-fungal agents in their manufacture. The limited prior art approaches of coating fibers and/or fabrics with anti-microbial or anti-fungal materials have had only limited success.

[0051] Home furnishings are not subjected to as much wear and tear as institutional furnishings and are usually made of a material which has a softer "feel" and is usually more delicate than those made for institutional use. Therefore, it is difficult to make such materials which will stand up to repeated washings and to wear, particularly when they have been prepared with additives for special properties such as anti-microbial agents.

[0052] Thus, there still exists a need to develop fabrics, materials and surfaces substrates for use in home and institutional furnishings which contain metal-containing anti-microbial agents that do not cause the development of resistant bacterial strains for incorporation into fibers that are used to make a variety of fabrics. There also still exists a need for these anti-microbial agents to be resistant to being washed away, thus maintaining their potency as an integral part of the fibers, fabrics, materials, and furnishings into which they are incorporated.

SUMMARY OF THE INVENTION

[0053] It is an object of the present invention to provide anti-microbial agents that are efficacious and greatly resistant to washing off or wearing off of the product to which they are applied.

[0054] It is also an object of the present invention to provide anti-microbial additives that are inorganic.

[0055] It is another object of the present invention to provide a fiber with anti-microbial properties in which the anti-microbial agent is applied to certain areas, or has higher

concentrations in certain areas, to reduce the amount of the anti-microbial agent which needs to be used and thus lower the cost of such fiber and/or a product including such fiber.

[0056] It is another object of the present invention to provide an anti-microbial fiber combined with non-anti-microbial fibers for use in anti-microbial finished products that are able to withstand significant wear and washings and still maintain their effectiveness.

[0057] It is a further object of the present invention to provide an anti-microbial fiber:

combined with color pigments for coloration for the use in anti-microbial finished products to withstand fading;

combined with UV additives to withstand fading and degradation in products exposed to significant UV light;

combined with additives to make the surface of the fiber hydrophilic or hydrophobic;

combined with additives to make the product flame retardant or flame resistant;

combined with additives to make the product anti-stain; and/or

using pigments with the anti-microbial so that the need for conventional dyeing and disposal of dye materials is avoided.

[0058] These and other objects of the present invention are accomplished by synthetic fibers having anti-microbial and/or anti-fungal properties using various thermoplastic polymers blended with other types of fibers, and additives, some incorporating natural fibers.

[0059] Thus, the present invention provides a synthetic anti-microbial fiber comprising high and low levels of various thermoplastic polymers and controlled concentrations of inorganic anti-microbial additives mixed with polymers and selectively placed in the end product for greatest technical effectiveness and cost effectiveness.

[0060] The anti-microbial and/or other agent(s) are held in the sheath and are exposed externally by suitable sizing of particle cubes and sheath thickness, e.g., using one micron cubes and 2 micron thick sheaths, and similar ratios of sheath to core in other sizes.

[0061] The present invention also provides a synthetic anti-microbial fiber comprising high tenacity polymers e.g. polyesters, polyethylene terephalate (PET) in one portion and hydrolysis resistance polymers in another portion with hydrophilic and anti-microbial additives. In some applications the latter portion can be deliberately made hydrolysis-vulnerable to allow "blooming" and enhanced access to anti-microbial additives in the course of several washings or extended uses.

[0062] The various polymers, include but are not limited to, polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), PCT, PETG [PET, type G], Co-PET and copolyesters generally, Styrene, polytrimethylene terephalate (PTT)m 3GT, Halar®, polyamide 6 or 6,6, etc. The additives include pigments, hydrophilic or hydrophobic additives, anti-odor additives and anti-microbial/anti-fungal inorganic compounds, such as copper, zinc, tin and silver.

[0100] After heat activation, the PETG fiber melts, wets the surface of the surrounding fibers, and settles at the crossing points of the fibers, thus forming "a drop of glue" which bonds the fibers together and distributes the anti-microbial additives.

[0101] The excellent wetting characteristics of PETG can be used to distribute the anti-microbial additive uniformly within a product. In addition to the zeolite of silver, the PETG could carry other inorganic anti-microbial additives such as copper, zinc, or tin.

[0102] In addition to the anti-microbial component, the invention may be used to carry pigments with the PETG to achieve certain colors without the need to dye the other fibers.

[0103] The created synthetic fibers of polymers and additives can further be blended with non anti-microbial fibers to provide anti-microbial finished products that are able to withstand significant wear and washings and maintain their effectiveness.

[0104] The use of hot water improves the products in that washing the fibers/products in hot water opens the pores of the PET and such washed products perform better than unwashed products (this is thought to be due to the removal of spinning/weaving lubricants).

[0105] Material can be made in biodegradable form, such as by adding corn starch to the core or sheath polymers. This enables whole families of disposable fibers/products.

[0106] PETG may be used as one of the polymer blends and/or carriers for a wide variety of applications. PETG is an amorphous binder fiber that can be blended into yarns with other fibers to form woven fabrics, as well as knits and non-woven fabrics. It has two characteristics of particular interest: (1) excellent wetting and (2) low melting temperature (which can be controlled between 90°C and 160°C). It is used in the present invention as a carrier to carry pigments and/or anti-microbial additives and/or other additives and is blended with other fibers which may be natural fibers such as cotton, silk, flax, wool, etc. or other synthetic fibers such as : PET, PP, PE, Nylon, Acrylic, etc. After heat activation, the PETG melts, continuously releases the color pigments and/or anti-microbial or other additives and wets the surface of the surrounding fibers with the pigment and/or anti-microbial or other additives it carries. It settles at the crossing points of the fibers, thus forming "a drop of glue" which bonds the fibers together. Therefore, PETG delivers and distributes the pigments and/or anti-microbial or other additives uniformly within a fabric, generating the finished fabrics and/or fabrics having anti-microbial properties.

[0107] Since the natural fibers used to blend with PETG are not changed physically after heat activation of PETG, they contain the same characteristics as natural fibers. The PETG may be used together with or without anti-microbial agents to form a product having excellent color fastness even in the presence of sunlight, and will withstand many washings without deterioration. The product is made by blending PETG used as a carrier for pigments and/or anti-microbial additives, with cotton or any other fibers of synthetic material such as from polyester and rayon, and activating PETG from 110° to 140° C. The color is thus provided to the yarn and product without the need of going through a dye bath. This product remains color- fast for in excess of 50 commercial launderings.

[0108] The excellent wetting characteristics of PETG can be used to distribute the pigments and/or anti-microbial additive uniformly within a yarn or product. While many anti-microbial agents may be used, such as those, which use copper, zinc, or tin, the preferred agent is zeolite of silver. In addition to the anti-microbial component and the pigment added to the PETG, the PETG may be used as a carrier to add other properties to yarn and other products, such as fire retardants.

[0109] It is a principal object of the footwear components embodiment to provide such footwear components that meet these needs in a manner consistent with industry specifications, overall durability, and cost-effectiveness.

[0110] It is another object of the footwear components embodiment to provide such footwear components in various forms such as rigid, semi-rigid or flexible and which may be constructed using fibers or not as desired.

[0111] A further object of the footwear components embodiment is to have the anti-microbial agent as close as possible to a person's foot.

[0112] An additional object of the footwear components embodiment is to have a higher concentration of the anti-microbial and/or anti-fungal agent close to the surface and not wasted by being placed into other parts of the where the anti-microbial property is not needed..

[0113] The foregoing objects are met by footwear components such as insoles, midsoles, box toes, counter and linings of footwear products, e.g., shoes, slippers, sneakers and the like in which the anti-microbial agent is available for the life of the product and not washed away or worn away by sweat or abrasion. Also, the anti-microbial agent is placed into the component close to or on the surface which is most needy of the protection, such as the part of an insole closest to the foot of a user when the insole, or other component is assembled into a footwear product. Thus, the fungi or microbes which may form and create odors or other problems are killed on contact with the surface of the shoe component anti-microbial surface area.

[0114] The footwear component of the disclosed products can be a nonwoven fabric of synthetic fibers, primarily polyester, but which could be acrylic, nylon, rayon, acetate, PP, and the like. The fabric can have a weight from 65-400 grams per square meter and typical fibers range from 1.2 dTex to 17 dTex with a cut length of 15-180 mm. They are carded, cross-lapped and needle punched, but could be produced on other types of nonwoven equipment, such as spun laced or spun bonded equipment.

[0115] The impregnation is a latex of SBR, vinyl acetate, PVC, acrylonitrile, and the like. Impregnation is from 1-4 times the weight of the nonwoven fabric on a dry basis. A range of fillers such as clay, calcium carbonate, and the like are used to reduce the cost. There are two

basic methods. One is to mix the anti-microbial with latex compound and impregnate it into the insole. The other is to use anti-microbial fibers on the insole in various manners.

[0116] The anti-microbial will usually be included at and near the surface of a thin layer such as a film. The concentration of the anti-microbial agent can be varied as a gradient using mixing strategies. The concentration of anti-microbial agent within or on the surface of sheet material can also be varied regionally using materials containing varying amounts of anti-microbial agents in conjunction with both natural and synthetic materials having different amounts of anti-microbial agents or even no added anti-microbial agents. A variety of other agents can be added, either by mixing or topically, to color the material and/or to make it resistant to staining, fire, and ultraviolet (UV) light as well as altering its water absorbing qualities. Various polymers, without limitation, can be used to form these fibers. In the context of this invention, anti-microbial refers, but is not limited, to antibacterial and anti-fungal.

[0117] The present invention provides several embodiments, one of which relates to the co-extrusion of flat or shaped films or profiles. The product may be a multi-layer construction with the surface layer, on one or both sides, containing zeolite of silver (or other metal such as tin, copper, zinc, etc.).

[0118] The product may be a flat film for use in a flat form for counter tops, floors, walls, or molded into shapes such as cafeteria trays, serving dishes, high chair table, refrigerator trays, microwave liners, and luggage.

[0119] The same concept applies to multi-layer injection molded parts. In this case the surface layer may have anti-microbial properties in applications such as telephone handsets, baby bottles, computer keyboards, plastic utensils, and milk bottles.

[0120] The choice of particle size of the zeolite is based on the thickness of the film to obtain the best combination of surface area with anchoring in the film. For example, a very thin film of 3 m would be best served with a 1-2 m zeolite, which would have a maximum dimension of 2 x 1.73 or about 3.5m.

[0121] The inner films could be made of basically any thermoplastic resin, such as; PE, PP, PET, PS, PCT, Polyamide (nylon), Acrylic, PVC, etc. The surface layer(s) could be made of the same polymers plus some low temperature ones such as PETG, Polycaprolactone, EVA, etc.

[0122] Home and institutional furnishings are provided which are made from fibers, yarns, fabrics, materials, and substrates having anti-microbial properties using inorganic silver-containing compounds. This allows, for example, the formation of both mono- and multi-component polymeric fibers having these anti-microbial agents intermixed within the polymer during fiber formation. The concentration of the anti-microbial agent can be varied within each individual fiber as a gradient using mixing strategies and also from fiber to fiber. The concentration of anti-microbial agent within a fabric or material made from these anti-microbial fibers can also be varied regionally using fibers containing varying amounts of anti-microbial agents in conjunction with both natural and synthetic fibers having different amounts of anti-microbial agents or even no added anti-microbial agents. A variety of other agents can be added, either by mixing or topically, to color the fibers and/or to make it resistant to stains, fire, and ultraviolet (UV) light, as well as altering its water absorbing qualities. Various polymers, can be used to form these fibers. In the context of this invention, anti-microbial refers, but is not limited, to having anti-bacterial and anti-fungal properties.

[0123] The concentration of the anti-microbial agent can be varied within each individual fiber as a gradient using mixing strategies and also from fiber to fiber. The concentration of anti-microbial agent within a fabric or material made from these anti-microbial fibers can also be varied regionally using fibers containing varying amounts of anti-microbial agents in conjunction with both natural and synthetic fibers having different amounts of anti-microbial agents. A variety of other agents can be added, either by mixing or topically, for different reasons, such as altering its water absorbing qualities. Various polymers can be used to form these fibers. In the context of this invention, anti-microbial refers, but is not limited, to anti-bacterial and anti-fungal.

BRIEF DESCRIPTION OF THE DRAWING

[0124] Other objects, features and advantages will be apparent from the following detailed description of preferred embodiments taken in conjunction with the accompanying drawings in which:

[0125] **FIGS. 1A, 1B, 1B', 1B"** and **1C** are cross-sectional views of various fiber configurations used in practice of the various embodiments of the invention;

[0126] **FIG. 2** is a sketch of a fibrous mass using one or more of the fibers of **FIGS. 1A-1C**;

[0127] **FIG. 3** is a schematic view of the feed hopper, screw and extruder;

[0128] **FIG. 4** is a sectional view through the exit of the extruder showing the formation of coaxial bi-component fibers of the present invention;

[0129] **FIGS. 5** and **6** are photomicrographs of fibers showing the particles of zeolite of silver;

[0130] **FIG. 7** is a schematic isometric view of a first type of insole using latex;

[0131] **FIG. 8** is a schematic isometric view of a second type of insole using a layer of anti-microbial fibers;

[0132] **FIG. 9** is a cross section through an insole made in accordance with the present invention;

[0133] **FIG. 10** is a plan view of the insole of **FIG. 9**;

[0134] **FIG. 11** is a cross section through a laminate for footwear components;

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

[0135] In the United States, all claims concerning anti-microbial and anti-fungal properties must be thoroughly tested to Environmental Protection Agency (EPA) and Food and Drug Administration (FDA) standards before making claims. The anti-microbial herein can be said to "kill bacteria" in that it kills 99.99% (log 4) of bacteria in 24 hours, and "anti-microbial" in that is kills 99.9% (log 3) of bacteria in 24 hours. This is based upon actual test results. Testing, such as

by using the shake flask test, has demonstrated that when fibers and fabrics are tested using the anti-microbial system disclosed herein, the number of bacteria on the fibers is reduced by 99.99% or more over a 24-hour period and at least by 99.9%. This testing was performed using several different bacteria, including Pseudomonas aeruginosa, Staphylococcus aereus and Klebsiella pneumoniae. The testing was conducted using both unwashed fibers and fibers that had been washed fifty times to simulate use of the fiber in an application, such as a pillow. The EPA has indicated that products tested using this system may claim "Prohibits Bacteria Growth and Migration Along the Surface of the Product." The addition of the agent in this system inhibits the growth of mold and mildew or odor-causing bacteria in the fibers. This is a true anti-microbial product. The fibers retain their efficacy after simulated use conditions so that the anti-microbial action lasts the life of the product.

[0136] *THE FIBERS AND THE ADDITIVES*

[0137] According to a first configuration of the present invention shown in **FIGS. 1A-2** a bi-component fiber **10A** is formed of a sheath component S and a core component C using polyethylene terephthalate (PET) (or other thermoplastic polymer) in the core, making up between 20 to 80 % of the fiber by weight. The sheath is also PET, or other thermoplastic polymer, making up between 80 to 20% of the fiber by weight including, as a dispersed solid, additive A (or compounded with the sheath plastic) an anti-microbial compound, to gain the efficiency of the additive on the surface and not wasting the additive in the core.

[0138] In the more generalized case as mentioned above, the sheath may be quite thin. However, preferably the sheath is more than 28% of the total fiber cross-section. It has been found that one of the best methods for retaining the anti-microbial qualities in the fiber and in fabrics is to use sheath thicknesses which are properly related to the size of the anti-microbial additive particles. For example, when the anti-microbial particles are approximately 1 micron cubes, which provides diagonal dimensions of approximately 1.7 microns, the sheath thickness would be in the vicinity of 2 microns. In this manner the particles of the agent are firmly held in

the sheath by the material of the sheath holding them in place. When the particles are larger or smaller, the thickness of the sheath is adjusted accordingly.

[0139] The anti-microbial/anti-fungal additives are inorganic compounds using such metals as: copper, zinc, tin, and silver. The best results are obtained using a zeolite of silver dispersed in a polyethylene (PE), PET, or polybutylene terephthalate (PBT) carrier, but could be added directly to a melt of a sheath thermoplastic without an intermediate carrier. The total anti-microbial additive ranges from 0.2% (0.002) to 6.0% (0.06) by weight of fiber depending on performance requirements. The anti-microbial additives are held in the sheath and are prevented from washing off over time and remain effective, especially when the sheath-thickness to agent-particle size ratio is in a desirable range as mentioned above and discussed in more detail below.

[0140] The bi-component anti-microbial/anti-fungal synthetic fiber size would preferably range from 0.7 dTex to 25.0 dTex and could be produced as a cut staple fiber in lengths from 1.0 mm to 180 mm, or in a continuous filament.

[0141] Additives which can be incorporated include one or more of UV stabilizers at 0.1% (all %'s herein are by weight unless otherwise stated) to 5.0%; fire retardant (FR) additives at 0.1% to 5.0%; pigments at 0.1% to 6.0%; hydrophilic additives at 0.2% to 5.0%; hydrophobic additives at 0.2% to 5.0%; and/or anti-stain additives at 0.2% to 5.0%.

[0142] A second configuration of this first embodiment of the present invention is a bi-component fiber **10B** in which the components x, y (x = strength, y = functional portion) are side-by-side and the same polymers and additives are used as described above. Variants of this are shown in **FIG. 1B'** in which the tri-component fiber **10B'** has components x1, x2 and y', and in **FIG. 1B"** in which the four-component fiber **10B"** has components x1, x2, y1 and y2.

[0143] A third configuration shown in **FIG. 1C** is a continuous filament **10C** that could be used by itself as the binder or as part of a yarn or fabric with cooperating (strength) fibers indicated at **10D**.

[0144] It should be understood that the nominal "binder" fiber or binder component can also be a strength enhancer in some combinations. It will also be understood that other variants with respect to **FIGS. 1A-1C**, including, but not limited to combinations, can be made. For example, a

first extrusion could produce intermediate fiber products as in **FIG. 1A** and such products could be put together with each other or separate strength fibers and processed to produce simulations of **FIGS. 1B, 1B'. 1B", 1C**.

[0145] **FIG. 2** shows a non-woven or woven fibrous mass M made up of any of the fibrous configurations of **FIGS. 1A-1C** after heating wherein the binder fiber component melts and flows to form locking knots at many (if not most or all) of the cross-over points or nodes N of the fibrous mass to enhance strength and durability of the mass while maintaining a dispersion of the binder materials and its functional additive(s).

[0146] While the preferred embodiment is a PET/PET bi-component with zeolite of silver being used only in the sheath. Resins with different viscosities can be used to obtain improved performance. A PCT/PET arrangement is one variation which takes advantage of the hydrolysis resistance and resilience; however, the PET/PET is more cost effective, especially for use in apparel and bedding.

[0147] **FIGS. 1A-2** can also be used to describe a second embodiment grouping of practice of the invention.

[0148] The first configuration of the second embodiment of the present invention is a bi-component fiber of a core and a sheath as shown in **FIG. 1A** using PET or other high tenacity polymer in the core at between 20% and 80% by weight of the fiber. Poly 1,4 cyclohexylene dimethylene terephthalate (PCT) or other hydrolysis resistant polymer is used for the sheath at 80% to 20%. The core is designed to provide the strength of the fiber and the modulus can be varied to create a high modulus fiber with properties of high tenacity and low elongation similar to cotton, or a low tenacity and higher elongation fiber with properties similar to wool; or anywhere in between to obtain different fibers to make them as compatible as possible for their end uses and for any blend in which they will be used. In fibers, modulus refers to the area under the curve in a stress/strain curve. The sheath is preferably over 28% of the total cross sectional area. The sheath uses PCT which provides a hydrolysis resistant surface with good wrinkle resistance and resistance to long term washings in boiling water and strong soaps.

[0149] Additives in this second embodiment include pigments, compounds to create a hydrophilic surface, and anti-microbial, anti-fungal, anti-odor additives. The pigment additives are to provide uniform colors that do not fade significantly over long-term use and washing, unlike dyes. Compounds may be used which create a hydrophilic surface and this is designed to wick body moisture away from the skin and evaporate to create comfort for a wearer of a garment containing such fibers and is particularly useful for career apparel such as uniforms, work clothes, etc. The anti-microbial, anti-fungus and anti-odor additives can be varied depending on the functionality of the career apparel.

[0150] The bi-component anti-microbial/anti-fungal synthetic fiber size ranges from 0.7 dTex to 25.0 dTex and can be produced as a cut staple fiber in lengths from 1.0 mm to 180 mm, or in a continuous filament.

[0151] Another arrangement (**FIG. 1C**) is a bi-component continuous filament that could be used by itself or as part of a yarn or fabric.

[0152] **FIGS. 1A-2** can also be used to describe a third embodiment grouping of practice of the invention.

[0153] The third embodiment of the invention is a mono-component of homo-polymer fiber made from low temperature polymers with a melting or softening temperature below 225° C. such as PETG. It relates to a binder fiber carrier for anti-microbial additives, which can be further blended with non-anti-microbial fibers to provide an anti-microbial finished fabric that is able to withstand significant wear and washings and maintain their effectiveness. The anti-microbial additives are inorganic.

[0154] A mono-component or homo-polymer fiber used in this embodiment was made from low temperature polymers with a melting or softening temperature below 225° C. such as PETG (PET modified with 1,4, cyclohexanedimthanol), PE, PP, co-PET, or amorphous PET. Another low melting temperature polymer which may be used is polycaprolactam (PCL). The anti-microbial additives are inorganic compounds made from metals such as copper, tin, zinc, silver, etc. The preferred compound is a zeolite of silver dispersed in PE, PET, or PBT before being added to the fiber. The additives could be added directly to the primary polymer with pre-

dispersion. The total active ingredients range from 0.1 to 20% by fiber weight. Other inorganic metals such as tin, copper, zinc, etc. work also but not as well as zeolite of silver.

[0155] The binder (carrier) fiber containing polymers and anti-microbial additives can be blended with non anti-microbial natural fibers such as cotton and wool, or synthetic fibers such as polyester, acrylic, nylon, PTT, 3GT, rayon, modified rayon, and acetate to an anti-microbial finished fabrics that is able to withstand significant wear and washings and maintain their effectiveness.

[0156] A typical example is a fiber using the PETG polymer with the zeolitic contained silver additive blended with cotton up to 10% by weight to produce a bed sheet. The binder fiber is activated in the drying cycle of the final bleaching operation or other heat operation. The PETG melts and wets the surface of the cotton fibers to carry the anti-microbial characteristics to the entire sheet with an added benefit of increasing strength and reducing pilling.

[0157] The fiber size ranges from 0.7 dTex to 25 dTex and a staple length of 1.0 mm to 180 mm. A continuous filament yarn can also be produced that can be used in a wrap spun application whereby non-anti-microbial fibers are spun around the anti-microbial filament.

[0158] The antimicrobial product withstands more than 50 commercial washings at 80° C and/or dry cleanings. It is immune to UV exposure of at least 225 kj. It possesses excellent abrasion resistance and is unaffected by tests such as Tabor or Wyzenbeek.

[0159] The present invention also provides a unique way to use polymers such as PETG to carry and deliver anti-microbial additives and/or pigments to a natural non-anti-microbial fiber, such as cotton, wool, possibly mixed with polyester, nylon and the like, and generate a final binding fabric having anti-microbial properties.

[0160] PETG has two characteristics of interest: (1) excellent wetting and (2) low melting temperature. In the present invention, it is used as a carrier to carry anti-microbial additives and be blended with non-anti-microbial fibers. After heat activation, the PETG melts, continuously releases the anti-microbial additives and wets the surface of the surrounding non anti-microbial fibers with the anti-microbial additives it carries. Thus, PETG delivers and distributes the anti-microbial additive uniformly within a fabric and the PETG holds the anti-microbial agent in

place, generating the finished fabrics having anti-microbial property. Since the natural fibers used to blend with PETG are not changed physically in this process, they contain the same characteristics as natural fibers.

[0161] The bi-component fiber may be formed by the use of pellets of the two different polymers or a direct polymer stream from the reactor of which the fiber is to be formed. The arrangement shown in **FIG. 1A** is intended for a configuration of a core fiber, and a sheath fiber which contains an additive, e.g., an anti-microbial agent. Since the best of the anti-microbial agents known at this time to the present inventor is zeolite of silver, the present example uses this agent. The intent is to use the minimum amount necessary to provide the desired characteristics. The additive provides the desired anti-microbial effect only at the surface. Therefore, if the bulk of the additive is located within the volume of the fiber well below the surface, that portion will not be useful for most or all of the life of the material into which the fiber is made. Since there frequently is some surface abrasion, some of the additive particles which are just below the surface when the fiber is made, become available at the surface, later in the life of the product.

[0162] In the past, attempts have been made to provide the additive at the surface, and the result was that the additive particles did not have a very useful life since they were removed from the surface by washing and wear or use. Therefore, the present invention strongly attaches the additive particles to the outer region of the fiber.

[0163] It has been possible to make particles of zeolite of silver as small as 1 micron cubes. A particle of such size will have a diagonal dimension of about 1.7 micron. Therefore, the smallest thickness of the sheath would be about 2 microns. The present invention permits a core/sheath arrangement in which the sheath is as small as 2 microns in thickness with the additive incorporated into the sheath. The diameter of the sheath is adjusted to the particle size so that the particles are held firmly in place and are available at the surface of the sheath. The particles may be smaller or larger than 1 micron cubes or larger, and the sheath may be correspondingly smaller than 2 microns or larger. In such an arrangement most, or all, of the additive is available for surface action, and, with wear and/or washings a small amount of the surface of the sheath will wear or wash away, and other additive particles which were originally more deeply embedded, become available at the surface.

[0164] The photomicrographs of **FIGS. 5 and 6** show the small particles of zeolite of silver in the sheath, many of which can be seen on the surface or projecting through to the surface of the fibers. There are more such particles which are just below the surface of the fibers, and which will become available for anti-microbial activity as small portions of the fiber wears or washes away and the particles become available at the surface.

[0165] **FIGS. 3 and 4** show a manner of making a core/sheath fiber with an anti-microbial additive which is incorporated into the sheath polymer prior to the final extruding of the fiber. In the prior art, this was mostly done as a treatment after extruding.

[0166] The extruder **12** is shown diagrammatically in **FIG. 3** having a feed hopper **14**, an extruder screw section **16** for feeding melted material to the delivery end, and a heating chamber **18** which surrounds the bottom of the feed hopper as well as the total length of the extruder screw section **16** for melting the pellets which are fed into the hopper and maintaining the polymers in melted condition for being extruding through the extruding openings which act as nozzles. Besides pellets, it is possible to make these fibers using direct polymer streams from continuous reactors feeding to the melt pumps for a company which is a polymer producer.

[0167] There are two extruders, one which has a feed hopper for forming the sheath and another with a hopper for forming the core.

[0168] The nozzle end of the extruder is shown in cross section in **FIG. 4** which includes three sheets of metal **20, 22** and **24** to form two chambers **26** and **28**. The melted polymer is fed into the extruder nozzle from the top. There are a plurality of two types of holes, one type being **28** and which feeds into chamber **26** to form the core of the fiber, and the other type being **32** which feeds into chamber **28** to form the sheath of the fiber.

[0169] The following non-limiting examples illustrate practice of the invention.

<u>*Example 1*</u>

[0170] The anti-microbial fiber of the present invention was used in the making of a mattress pad. In this example, 15% of a 6.7 denier 76mm cut length natural white fiber was used as a homofilament with zeolite of silver as the anti-microbial agent and 15 % of a bi-component fiber

was used together with 70% PET 6x3 T295 in a blend in which the zeolite of silver comprised 0.9% of the fiber. The blend of this fiber was made into a batt of about 1-1 1/2 " thickness of nonwoven material which was then placed between two layers of woven fabric to form a mattress pad. When tested using the shake flask test this provided a 99.99% microbial kill ratio.

[0171] There are other examples in which all of the parameters of Example 1 were used and in each of which there was 15% of a bi-component fiber used. Again the zeolite of silver comprised 0.9% of the fiber. The percentage of the anti-microbial fiber ranged from 20% to 40% and the PET ranged from 45% to 65%. In all examples the microbial kill ratio was 99.99% using the shake flask test.

<u>Example 1A</u>

[0172] In this example, 35 % of a 6.7 denier 51mm cut length natural white fiber was used in a sheath/core bi-component configuration with zeolite of silver as the anti-microbial agent and 15% of another bi-component fiber was used together with 50% PET 6x3 T295 in a blend in which the zeolite of silver comprised 1.8% of the fiber. The blend was then prepared as in Example 1 and when tested using the shake flask test, there was a 99.9% microbial kill ratio.

[0173] A second group similar to the first one was prepared in which the sheath/core bi-component fiber with zeolite of silver as the anti-microbial agent comprised from 10 to 35% of the fiber blend, 15% of another bi-component fiber was used and from 50 to 75% of PET 6x3 T295 was used. The zeolite of silver comprised 0.75% of the fiber. In the shake flask test, there was a 99.99% microbial kill ratio.

<u>Example 2</u>

[0174] In this example, 15% of a 3.5 denier 38mm cut length PETG fiber was used as a homofilament with zeolite of silver as the anti-microbial agent. 85% PET fiber was blended with the PETG anti-microbial fiber to form a blend in which the zeolite of silver comprised 1.8% of the fiber. The fiber was made into a wall covering and was tested by the shake flask test, which provided a microbial kill rate of 99.99%

[0175] A modified version was prepared the same way except that there was only 10% fiber with zeolite of silver in the blend and 90% PET fiber was used. After the fiber was made into a wall covering, this too provided a 99.99% microbial kill rate using the shake flask method of testing.

[0176] A further modified version was used in which there was only 5% fiber having zeolite of silver in the blend and 95% PET fiber in the blend. The testing, after the fiber was used in a wall covering, again provided a 99.99% microbial kill rate for bacteria.

[0177] The fibers described above can be used to make both woven and nonwoven fabrics as well as knitted fabrics. Such fabrics are useful for various types of articles, some of which are listed below.

FOOTWEAR COMPONENTS

[0178] Footwear components as disclosed, for example, in pending provisional application Serial No. 60/181,251 filed February 9, 2000, the contents of which are physically incorporated herein below, in which the footwear components provide several embodiments of anti-microbial and/or anti-fungal footwear products. The footwear components such as insoles, midsoles, box toes, counter and linings of footwear products, e.g., shoes, slippers, sneakers and the like are provided in which the anti-microbial agent is available for the life of the product and not washed away or worn away by sweat or abrasion. Also, the anti-microbial agent is placed into the component close to or on the surface which is most needy of the protection, such as the part of an insole closest to the foot of a user when the insole, or other component is assembled into a footwear product. Thus, the fungi or microbes which may form and create odors or other problems are killed on contact with the surface of the shoe component anti-microbial surface area. The footwear components can be a nonwoven fabric of synthetic fibers, primarily polyester, but which could be acrylic, nylon, rayon, acetate, PP, and the like. The fabric can have a weight from 65-400 grams per square meter and typical fibers range from 1.2 dTex to 7 dTex with a cut length of 25-76 mm. They are carded, cross-lapped and needle punched, but could be produced on other types of nonwoven equipment, such as spun laced or spun bonded equipment. The impregnation is a latex of SBR, vinyl acetate, PVC, acrylonitrile, and the like. Impregnation is from 1-4 times

the weight of the nonwoven fabric on a dry basis. A range of fillers such as clay, calcium carbonate, and the like are used to reduce the cost. There are two basic methods. One is to mix the anti-microbial with latex compound and impregnate it into the insole. The other is to use anti-microbial fibers on the insole in various manners.

[0179] The footwear components are provided by several embodiments described herein but may be practiced using other embodiments. There is described below, a first embodiment of a single layer of latex, and a second embodiment of a main support layer and a fiber layer attached thereto.

[0180] The foregoing objects are met by footwear components such as insoles, midsoles, box toes, counter and linings of footwear products, e.g., shoes, slippers and sneakers in which the anti-microbial agent is available for the life of the product and not washed away or worn away by sweat or abrasion. Also, the anti-microbial agent is placed into the component close to or on the surface which is most needy of the protection, such as the part of an insole closest to the foot of a user when the insole, or other component is assembled into a footwear product. Thus, the fungi or microbes which may form and create odors or other problems are killed on contact with the surface of the shoe component anti-microbial surface area.

[0181] The footwear component can be a nonwoven fabric of synthetic fibers, primarily polyester, but which could be acrylic, nylon, rayon, acetate, PP, and the like. The fabric can have a weight from 65-400 grams per square meter and typical fibers range from 1.2 dTex to 17dTEx with a cut length of 15-180 mm. They are carded, cross-lapped and needle punched, but could be produced on other types of nonwoven equipment, such as spun laced or spun bonded equipment.

[0182] The impregnation is a latex of SBR, vinyl acetate, PVC, acrylonitrile, and the like. Impregnation is from 1-4 times the weight of the nonwoven fabric on a dry basis. A range of fillers such as clay, calcium carbonate, and the like are used to reduce the cost. There are two basic methods. One is to mix the anti-microbial with latex compound and impregnate it into the insole. The other is to use anti-microbial fibers on the insole in various manners.

[0183] An embodiment of a nonwoven fabric impregnated with latex is shown in **FIG. 7** in which there is an insole **54** having a toe portion **56** and a mid sole portion **58** and a heel portion **60**

all in a single piece construction. It is a suitable fabric which is then impregnated with latex to provide cushioning for wearer comfort. The anti-microbial, in this case zeolite of silver is mixed with the latex prior to impregnating the insole.

[0184] **FIG. 8** is another arrangement wherein a support and cushioning layer **62** is provided and which may be any of a number of materials which are used for insoles, but preferably one which of a nonwoven material. A fiber layer **64** made of fibers which have the anti-microbial agent disposed therein is attached to cushioning and support layer **62** by any suitable means. In this arrangement zeolite of silver is the anti-microbial agent. This can include an adhesive, but could also be accomplished by making the support layer of a polymer which is also used for some of the fibers and the fiber layer **64** is attached to the support layer **62** as the support layer is first delivered after being prepared and still retains the heat of preparation whereby the common polymer is hot enough to partially melt and then become bonded together.

[0185] Some anti-microbial agents are also anti-fungal agents. When agents do not perform both functions, a second agent will usually be used.

[0186] The choice of particle size of the zeolite is based on the thickness of the layer carrying it to obtain the best combination of surface area with anchoring in the layer. For example, a very thin layer of 3m would be best served with a 1-2m zeolite, which would have a maximum dimension of 2 x 1.73 or about 3.5m.

[0187] The inner layer(s) could be made of basically any thermoplastic resin, such as; PE, PP, PET, PS, PCT, Polyamide (nylon), Acrylic, PVC, etc. The surface layer(s) could be made of the same polymers plus some low temperature ones such as PETG, Polycaprolactone, EVA, etc.

[0188] It is preferable to have the layer closest to a wearer's foot have the anti-microbial and/or anti-fungal agent and be porous to perspiration to absorb perspiration.

[0189] In the event a support layer is used which is not fibrous, it is covered with a nonwoven fabric, the fibers of which have the anti-microbial agent therein. Such a layer can be thinner than the support layer. However, it is usually best if the layers used allow perspiration to be carried away from the wearer's foot for both comfort and health reasons.

[0190] The anti-microbial particles are bonded into the surface layer and remain there for the life of the material and provide anti-microbial properties for the entire time.

[0191] It is advantageous to have the anti-microbial agent only at the surface since this is the only area which comes into contact with microbes and fungi, and to have the agent located in other places is wasteful.

[0192] Anti-microbial fibers can be used to make the footwear products of the present invention where it is necessary or desirable to reduce bacterial and fungal growth and their resultant odor. In manufacturing these materials, any of the embodiments of fiber described can be used. Both the strength and resiliency of these materials is important. Any number of shaped designs could be used as appropriate.

[0193] Also, other modifications of the characteristics of these fibers and material beyond that of adding anti-microbial agents, including the addition of agents to increase or decrease hydrophobicity, would be useful. In addition, anti-odor additives may be particularly useful.

[0194] The relatively small size of the silver-containing zeolite compounds (2 microns and less) that are used in the manufacturing of the fibers allow these anti-microbial agents to be incorporated into fibers instead of being applied to them. Thus, because these anti-microbial agents are an integral part of the fiber, they are not washed away by perspiration or easily abraded away and the finished components, such as insoles, manufactured from them are able to withstand significant wear while maintaining their anti-microbial effectiveness.

[0195] Specifically, higher loading of the anti-microbial agents (up to 5 times) is used to more effectively act against fungi. This higher loading may be achieved by using various zeolites followed by heating the fiber polymer, e.g. PET, to between 180 and 228 degrees Fahrenheit in hot water which allows further metal loading or ion exchange to replace resident metal ions with another ion or mixture of ions. In addition, this would allow the zeolite at or near the surface of the fiber to be preferentially loaded with the metal ion or mixtures thereof that has the desired biological effect. These methods are particularly useful in reducing costs when expensive metal ions, such as silver, are used in these processes. Also, by adding certain metals, e.g. silver, at this point in the process and not having it present during the high temperature fiber extrusion process,

any yellowing or discoloration due to oxidation of the metal ion or its exposure to sulfur and halogens would be greatly reduced.

[0196] It is also possible to use these integrated anti-microbial compounds to make shoe components and products that have a varying distribution of the anti-microbial agent. For example, by varying the concentrations of the anti-microbial agent during mixture with the fiber-forming polymers, fibers having varying anti-microbial content can be formed which can then be added in varying amounts to form materials having varying concentrations of anti-microbial agents. In addition, the amount of anti-microbial present in the fiber itself can be varied, either lengthwise or in cross-section. Similarly, higher and lower concentrations of these anti-microbial agents in the overall fibers can be achieved by using multi-layered sheets in which, for example, the anti-microbial agent is present only in an outer layer section, thus significantly reducing manufacturing and selling costs. Any of the above manufactured anti-microbial fibers can be mixed with fibers that do not contain anti-microbial agents such that products can be made having overall and localized variations in concentrations of anti-microbial agents.

[0197] In addition, the fibers can be made either hydrophilic or hydrophobic as desired by mixing other agents into the fiber polymers or applying them to the fiber surface. By modifying the wetability characteristics of the fibers, they can be made more useful for various applications. For example, hydrophilic fibers are effective in applications in which one wants the anti-microbial material to more easily absorb water, such as when the material is designed to be used in footwear. Alternatively, hydrophobic films or fibers are effective in applications in which one wants to avoid the absorption of such solutions. For example, the insole of the present invention could be made with a hydrophilic agent on the upper surface which will be nearer to the foot of the wearer, while the lower surface which will be adjacent other parts of the footwear, could be made with a hydrophobic to keep the perspiration away from other parts of the footwear.

INSOLES

[0198] A further embodiment of practice of the invention is shown in **FIGS. 9** and **10** wherein an insertable innersole **210** for shoes and boots is made up of multi-layers indicated in **FIG. 9**. The layering is indicated before heating and pressing this laminate to form a bonded construction.

The innersole has anti-microbial that are available in the as fully manufactured product and ,as in other embodiments of the invention described above, are provided in a cost efficient way.

[0199] A top layer **212** of the laminate is made of a non-woven or woven array of fibers, preferably of polyester, has an overall weight of 2.5 to 6.0 oz. per square yard and includes some 5 – 25 % of its weight as fibers that are mono-component or multi-component and incorporate zeolites of silver or other anti-microbial dispersed substantially uniformly in the layer. In eventual processing the surface **213** gets treated by embossing, ultrasonic bonding and/or other modification and the layer as a whole is heated (along with heating and pressing the laminate as a whole) to effect, among other things, bonding of fibers at many cross over points (nodes) **212N** in a manner well known in the art to effect densification and strength while retaining substantial porosity and moisture vapor permeability through the layer.

[0200] The next major layer **214** is made of thermo-formable polymers, preferably polyesters and/or co-polyesters including 20 – 80 weight percent of mono-component fibers and conversely 80 – 20 weight percent of multi-component fibers, the latter incorporating anti-microbial agents as described herein, the layer weight in 2.5 – 9.0 oz. per square yard. The layer is non-woven needle-punched fabric with some distinct fiber orientation in the lateral direction within layer **214** itself and with punched through fibers from the next lower layer as described below. This layer **214** is bonded to layer **212** by a an adhesive web of scrim or mesh form of 15 – **28** gm per sq. meter weight (very diaphanous) and made of polyester, polyolefins (polethylene, polypropylene, etc.), polyamide or other fiber materials and in the course of laminate heating and pressing becomes an effective bonding agent to bond layers **212, 214** securely to prevent de-lamination in service use.

[0201] The next major layer **216** is designed as a moisture storage (and eventual off-gassing) layer with high surface area fibers, including 20 – 50 weight percent of 4DG lobed or grooved fibers of polyester or other fiber material of a type well known per se, 50 – 60 weight percent of normally surfaced polyester mom-component fibers and 5 to 25 weight percent of bi-component fibers containing anti-microbial agents. The bi-component fibers are preferably normally surfaced but could also be made of grooved form, consistent with the missions of anti-microbial agent carriage and access. The layer as a whole weighs 4 – 12 oz. per sq. yard and is bonded to layer

214 by deep needle-punching fibers of layer **216** into layer **214** using barbed felting needles to establish lateral wicking paths as indicated, e.g., at **216L**.

[0202] The final layer **218** is a co-extruded two part plastic film with a barrier sub-layer portion **218A** and a bonding sub-layer portion **218B**, each such portion being 25 – 100 microns thick and made of A/B combinations of, e.g., polypropylene/polyethylene, polypropylene/polyester, polyropylene/polyamide, etc.

[0203] When the laminate is heated and pressed under state of the art conditions for molding such materials the layer **214** becomes highly densified and entraps the lateral fibers **216L** to secure layers **214, 216** together while bonding layers **215** and **218B** secure the outermost layers to the laminate.

[0204] The tough upper layer **212** resists cracking and shedding under the impact of direct user contact and flexing in use or when removed from a shoe but allows free flow of moisture vapor which is wicked through layer **214** to moisture storage layer **216** in an efficient way and retained there because of the bonded on moisture barrier **218A** so that odor doesn't go beyond the innersole to any substantial degree. The overall result is an odor absorbing innersole of fibrous material that provides necessary cushioning in a slim profile that can fit comfortably in an athletic or dress shoe or boot or moccasin/loafer. No foam materials or charcoal adsorbents or the like need be used. Moisture can be absorbed in the present product and retained with high destruction of odor causing microbes and the moisture can desorb gradually with lowered concentrations of odor causing microbes with two to three order of magnitude reduction.

MOLDABLE LAMINATES

[0205] Moldable laminates for footwear may also be produced as part of the present invention. A binding agent is provided in a nonwoven product in which the binding agent is a thermoplastic binder fiber or bi-component binder fiber. The binder fiber is thermally activated in order to bind (stiffen) the nonwoven portion of the product. Since this is produced with 100% thermoplastic components allows for easy recycling. The product is a thermal moldable impact resistant stiffener for footwear applications such a counter or box toe.

[0206] A 100% thermoplastic, stiff reinforcing multiple laminate structure which can be moldable into complex, compound shapes and bondable via a thermoplastic hot melt adhesive to a carrier surface to be reinforced to provide a tough, water resistant reinforcement, usable for instance in stiffening applications as a footwear counter or box toe reinforcement element that is recyclable into itself. The fabric layer is in part geometrically locked into the tough thermoplastic resin layer.

[0207] As shown in **FIG. 11**, the product comprises a tough extruded core of thermoplastic resin such as ionomer, EVA or styrene stiffened ionomer and at least one impact resistant strength layer of nonwoven.

[0208] The needle punched nonwoven is manufactured from a bi-component staple fiber or blend or PET staple fiber and binder staple fiber or blend of PET staple fiber and bi-component staple fiber. The nonwoven utilizes a combination of PET fibers and PETG or other copolymer or homopolymer fibers that act as a binding agent for PET. The staple fiber is 4-15 denier and 38 to 76 mm in length.

[0209] The thermoplastic components of the product are either miscible or mechanically compatible so as to allow for homogenization and incorporation into the extruded thermoplastic core thus allowing for complete recyclability of scrap material.

[0210] The binder fibers have a low melting temperature, and the fiber portion of the product is prepared as disclosed elsewhere herein.

[0211] It will now be apparent to those skilled in the art that other embodiments, improvements, details, and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

[0212] What is claimed is: